



WHITE PAPER

Issues Concerning Wall Deposits in the Chemical Analysis of Beryllium

Originated by the Sampling and Analysis Subcommittee

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What are they and why does it matter

The measurement of aerosol dusts has long been a method to evaluate the exposure of workers to metals. The various tools used to sample and measure aerosol dusts have gone through many transitions over the past century (1) and, in particular, there have been several different techniques used to sample beryllium, not all of which might be expected to have produced the same result (2). Today, samples are generally collected using filters housed in filter holders of several different designs. Some of the more recent designs of filter holders are expected to produce a sample that mimics the human capacity for dust inhalation. The presence of dust on the interior of cassettes used to hold filters during metals sampling has been noted. Particulates can enter the sampling cassette and deposit on the interior walls rather than on the sampling medium. The causes are not well understood but are believed to include particle bounce, electrostatic forces, particle size, particle density and airflow turbulence. Thus the question arises: if the worker is exposed to whatever particulate is in the air and if the filter does not catch all the particulate, “is the catch representative of the risk to the worker?” Wall deposition is not isolated to Beryllium nor is it an issue isolated to the DOE community. It has been demonstrated in many other metals and various groups are beginning to take a hard look at the implications of this issue. The purpose of this paper is to discuss some of the history, relevant issues and impact of this issue, what is currently being done by various groups, and future research needs.

History on samplers and sampling

In the early part of the 20th Century, particle concentrations were measured in terms of number, for example, millions of particles per cubic foot of air (mppcf). The impinger sampler was used for this purpose, as it collected aerosol dust into a liquid, from which a suspension of particles in a drop could be placed on a microscope slide for counting. All particles below a certain limit (e.g. 5 or 10 μm projected area diameter) were counted.

Mass is presently the preferred metric for chemicals with systemic toxic effects, and as is the case with many metals. The ability to accurately measure small masses of chemicals amidst larger quantities of background dust was provided by advances in analytical instrumentation. However, the cubic relationship between volume and diameter biases the importance of large particles as compared to the number metric so that particle size plays a role in determining the relationship between exposure assessments based on number and exposure assessments based on mass. Nevertheless the advantage of filters over inconvenient impingers, (for chemical analysis) is apparent when measuring mass.

In 1944, the U.S. Bureau of Mines compared filter sampling with impinger sampling (3), and in 1957, the U.S. Public Health Service (now NIOSH) revealed that they had been using membrane filter samplers for several years (4). At that time, they recommended the use of mixed cellulose-ester (MCE) membrane filters based on their

applicability to various analytical methods, including gravimetric, microscopic, and chemical analytical techniques. Early holders were made of stainless steel and were generally supports that exposed the filter to the air. They had the drawback of leaving the filter free to be tampered with or damaged. The plastic closed-face cassette (CFC), which houses 37 mm diameter filters, then known as the “Millipore Monitor”, was developed in 1956 for ANSA “clean-room” analysis, and appeared in the 1st edition of the American Conference of Governmental Industrial Hygienists (ACGIH) Air Sampling Instruments Handbook (5). The 4 mm entry inlet made the filter much less likely to be accidentally or deliberately damaged, which contributed to its growth in popularity. NIOSH Method S349 for “total dust” using the CFC was validated and published in 1977; with additional testing carried out in the early 1980’s to further investigate its sampling performance. Although further investigations (6, 7) concerning the performance of the CFC compared to the open faced cassette tended to solidify its preferences among practitioners, these evaluations did not compare the CFC with any performance standard for collection as one did not exist at that time for dust sampling. Throughout that intervening period, the main focus of workplace monitoring was on particles smaller than about 10 µm aerodynamic equivalent diameters (AED), which are sampled relatively efficiently by the CFC (7).

The concepts behind the inhalability of larger particles arose in the late 1980’s, and in 1993 a convention was agreed upon, that was based on a body of measurements of human inhalation efficiency, pushing inhalability to particles up to 100 µm AED. This is now referred to as the Inhalable Sampling Convention and was published in a standard, ISO 7708, (8) by the International Organization for Standardization Technical Committee 146, Sub-committee 2 (Workplace Air Quality). The ACGIH has accepted the ISO convention and proposed a number of “inhalable” threshold limit values, (TLVs, including one for beryllium,) based on this convention. Various samplers have since been tested for their aspiration efficiency against this model (9). The sampler that most closely matched the International Organization for Standardization (ISO) Standard for inhalability (ISO 7708) was the U.K. Institute of Occupational Medicine (IOM) sampler developed in 1986.

What is a sample?

Hence the issue of just what constitutes a sample has arisen. The issue as to whether or not particles collected on the walls of samplers are of significance was first brought to the Beryllium Health and Safety Committee (BHSC) through a review article by Harper and Demange (2). In their review they postulate that wall deposits, those particulates that impact and settle on the wall of a sampler and not on the filter, could be a significant part of sample aspiration for the CFC. This effect was first reported by the INRS in France (10), and in 1982 a Directive (11) published by the European Economic Community (EEC) was interpreted by the Institut national de Recherche et Securite (INRS) to mean that the sample included all particles that entered the cassette. Later, in the U.S., OSHA, in its sampling and analysis methods (12) included wall deposits in its gravimetric procedure and some of its chemical analyses procedures. In the *NIOSH Manual of Analytical Methods (NMAM)*, the concept of including wall deposits in sample analysis is discussed in the preamble to the manual, although a procedure for including these particles in the analysis is not specified nor required in any method (13). In 1986, in the development of a sampler designed to meet the ISO Inhalable Convention

wall deposits were considered to be an integral part of the sample. This sampler, designed at the U.K. Institute of Occupational Medicine (IOM), is known as the IOM sampler and includes wall deposits for gravimetric analysis. It was noted that, particles may be projected through the orifice of a sampler and impact the walls or fall through the orifice and onto the walls by gravitational settling; they may be attracted to the walls by electrostatic forces; or they may even bounce off the filter and onto the walls. Thus studies with this sampler recognized the addition of wall deposits and recommended that their presence be accounted for in the gravimetric analysis (14). In a French study in various metals industries (15), it was found the CFC results more closely matched IOM (inhalable) results when adding wall deposits. Several studies have been performed that compared performance of the CFC with the IOM inhalable sampler in both moving air (16) and calm air (17, 18, 19). When the mass of material on the walls of the CFC was added to that in the filter deposit, for samples taken side-by-side with the IOM sampler in various metals industries, it has been shown that differences between the CFC and the IOM “reference” inhalable sampler become much smaller at the finer end of the dust particulate range (< 15 μ m AED). However, the sampling efficiency dropped significantly for larger particles in the CFC (19).

Recent Actions by OSHA, AIHA , ASTM and the DOE community.

OSHA Salt Lake Technical Center (SLTC) has analyzed loose dust apparent to the eye in the cassette along with the sample filter since 1977. Method ID-125G was revised in 2002 to include specific instructions to rinse the cassette with DI water and to wipe out the cassette with a moistened clean filter to account for these deposits. OSHA analytical methods [ID-206](#), [ID-125G](#), [ID-121](#), [ID-105](#), that employ filter sampling for metals were modified in 2007 and requires wiping . In addition OSHA has performed some work to characterize the extent of the wall deposits in general metals samples (20, 21), and based on this, they have taken the position that air samples for metals should include all particles aspirated into the sampler. The OSHA SLTC laboratory now routinely rinses (when loose dust is present) and wipes the interiors of all cassette samples for chemical analysis of metals. It is unknown whether any new or revised standards will say anything about wall deposits.

The ASTM Subcommittee D22.04 on workplace Air Quality has advised users of analytical methods to determine whether the sample results need to include wall deposits. The details are provided in their non-mandatory appendices and they also provide guidance on ways to include wall deposits.

As for the DOE community, Lawrence Livermore National Labs has begun to include wall deposits in sample analysis but other labs have not.

What are the issues?

Several issues have been identified concerning the adoption of the convention of wiping of cassette walls for the inclusion of wall deposits. These issues fall into four categories: (1) issues of understanding what constitutes the sample (2) issues of understanding the significance of the wall losses and (3) issues of cost in implementing the change; (4) issues of data compatibility. These issues were identified by various members of the Beryllium Health and safety committee and are discussed below:

1. Issues of understanding what constitutes the sample

There are various opinions about what is the sample. Is it the filter catch, or should it include wall deposits (i.e. are wall deposits part of the sample)? Are the particulates that collect on the wall inhalable? Does the CFC collect the sample we need, or is biased low? Do the answers to these questions change with the analyte? Important questions that beg to be answered:

- Particle size and particle size distributions are of critical importance when considering sampling and analyses. There is currently no data on the effect of sampling ultra large ($> 100 \mu\text{m}$) particles or ultrafine particles and their impact on health. This question needs to be understood if as some researchers suggest, it is the larger particles that are collecting on the walls of the samplers.
- Similarly, static charge and humidity effects on particle size and collection efficiency, needs to be understood in order to understand and account for sample variability on the walls of cassettes when reporting results.
- The physical properties of the particles (spherical, fibrous, density, etc.) will have an impact on the amount of material deposited on the walls of samplers and needs to be understood.
- Sampling flow rates and sampling duration will need to be evaluated to assess the impact of wall losses for short term samples, full shift samples and multi-shift sampling.
- There is very limited data on beryllium and the impact of wall losses is unknown.
- Some of the inhalable samplers (such as IOM) are intended to include the deposits on the inlet and walls of the sampler. For gravimetric analysis this is straight-forward. For chemical analysis the manufacturer does not provide guidance on how to collect the particulate on the sampler walls.

2. Issues of understanding the significance of particulates that collects on the walls of the sampler:

- Adding wall deposits would increase the mass of the particulate being analyzed. Does that invalidate the current PELs and TLVs that were based on filter catch only? How do we compare “old” and “new” data in order to make recommendations on the impact of exposure after making such a change?
- Appropriate sample handling and digestion/extraction protocol (so that material is not lost from the walls) needs to be well defined.
- The method(s) used to remove materials from the walls of samplers will have to be evaluated and validated for accuracy and precision.
- Standard methods will have to be developed to ensure we can control for variability between labs and precision within labs.
- Wall wiping could introduce contamination from the additional handling of the sampler, or, additional handling could result in loss of sample.
- Additional media from wiping the walls of samplers could require a larger digestion volume, resulting in reduced sensitivity.

- The additional media could also contribute to a matrix effect that could interfere with the analysis.

3. Issues of the cost in implementing the change:

- There is also a cost issue associated with wiping the walls of cassettes when analyzing for beryllium. Removing materials from sampler walls would increase analytical costs (time and supplies). Within DOE alone cost can run in the millions of dollars per year. Any changes that increase the cost or the difficulty of sampling and analysis could decrease the number of samples collected or divert monies from other safety and health needs.
- In addition, AIHA requires the use of a validated Standard Method for any of its accredited labs. Any method that is modified must be identified and performance data is required before accreditation is rendered. Thus since methods “with” wall deposits have not been validated, the performance data could be required for anyone using that method. This would add additional cost to laboratories before they could perform such methods under their accreditation.

4. Issues of data compatibility:

Finally, there are issues related to defining an exposure and defining an exposure limit. The following issues are far more complex and are offered to promote a thoughtful perspective and to stimulate the potential for initiating applied research in this area.

- What is the relevance of the wall deposits to health risk?
- Is the contribution of wall losses significant to beryllium exposure profiles?
- What is the impact on epidemiology studies which has primarily been based on data that did not include wall deposits?

What are the Beryllium Specific Impacts?

Including wall deposits in the analysis of beryllium would likely affect many areas of the analysis. The main issue is that including wall deposits would likely result in an increase in beryllium levels found at a site. This could have a domino effect resulting in a corresponding increase in controls, personal protective equipment, medical surveillance, and ultimately cost in working with beryllium. While this is a good conservative approach, adding controls without the science to back the necessity of doing that could result in additional unintended risk to employees and cost to employers.

Path Forward

Although there may be some health-risk issues which may be associated/influenced by the contribution of the wall loss mass to the overall sample the data showing the relevance of the wall deposit fraction to health is just not yet available. Barring a thorough review of the data or any new data to shed some light on these issues there are currently three options that we could follow to address this issue of wall deposits: (1) do nothing, (2) change sampling methods, (3) change analytical methods.

Do Nothing – The first option is really to do nothing. To continue to use the published methods for collecting and analyzing a sample and to not include wall deposits as part of the sample unless it is a requirement of the method.

Change Sampling Methods – The second option is to identify sampling methods that reduce amount of particulates on the walls. There are several things we could do to the sampling device to help with wall deposits:

- Make the cassette conductive
- Create aerodynamically smooth surface
- Decrease diameter of filtration area
- Use the IOM sampler
 - Cartridge serves as sample inlet, sealed to filter
 - Would follow the inhalable convention
 - Would require a method developed to include all the particulate collected within the sampler.

Change sampling methods – The third option is to can change the methods to help with the inclusion of wall deposits. The methods currently in practice to include the wall deposits in the analysis include wiping the interior walls of cassette and including it in the digestion of the filter, or rinsing the cassette. However, these methods need to be validated and accuracy and precision demonstrated. If analysts are to follow the convention that wall deposits should be included in any analysis of beryllium exposure, it is clear that reliable, cost effective samplers that allow for reproducible digestion/extraction of all deposited particulates should be considered. The samplers should allow for the collection of particles in a completely digestible capsule, or should allow for easy and precise extraction of all the particles collected in the sampler, or should be designed to allow digestion/extraction inside the cassette. Some examples that have been suggested are:

- Redesign of cassettes to allow for easier access to the walls for wiping
- Material substitution to eliminate causative issues such as static charge or turbulence.
- Development of a fully digestible sample capsule that could be used for both gravimetric and chemical analysis of the sample.
- The development of better samplers. Inexpensive, disposable, “off the shelf” samplers for each of the ACGIH particle size fractions.
- Redesign cassettes to allow easy digestion/extraction inside the cassette. The French (INRS) have been doing this successfully for decades (7) and the technique standardized (see ISO15202)

Conclusions

Wall deposition of sample mass on the interior of cassettes during metals sampling has been a recognized phenomenon for many years. Even though the causes are not well understood, it is clear that the issues raised in this paper raise a legitimate concern and need further investigation and research. We know there are wall losses;

however, we need to let the answers evolve through data analyses before we alter existing sampling methodologies. It is the opinion of this group that it is premature for the BHSC to make a recommendation on the value of considering the use or non-use of wall deposits in determining exposure. Additional data is needed to fully determine if wall deposits are a relevant and significant beryllium sampling issue.

It is the recommendation of this group that a task force of the Beryllium Health and Safety Committee be formed to answer the question of “what constitutes the sample”. The mission of the task force will be to review all available data, and make a decision about where we stand with respect to what we know about a sample collected by CFC. The question to be answered is: “which of the following is true?”

- a) The inhalable fraction (as proposed by ACGIH in its NIC) is the correct fraction to obtain.
- (b) The inhalable fraction is not the correct (or most conservative) fraction.
- (c) We do not have data to support a conclusion of (a) or (b).

Once that data review and a recommendation is complete, wall deposition specific to beryllium, needs to be addressed in future research to answer some of the additional questions raised. Possible topics that could be pursued are:

- The significance and influence of wall deposits as they relate to beryllium exposure.
- Developing a recommendation on how to include wall deposits in sample analysis if they are concluded to be part of the sample.
- Assessment of the partition of field Be samples between filter and walls of the CFC.
- Validation of the recovery of wall deposits of Beryllium.
- Appropriate sample handling and digestion/extraction protocol (so that material is not lost from the walls).
- Evaluation of method(s) used to remove materials from the walls of samplers.
- Development of Standard Methods to control for variability between labs and precision within labs.
- Evaluation of contamination from the additional handling of the sampler, or, additional handling.
- Evaluation of costs associated with including wall deposits.

References

1. **Kolanz, M., Madl, A., Kelsh, M., Kent, M., Kalmes, R., Paustenbach, D. A** Comparison and Critique of Historical and Current Exposure Assessment Methods for Beryllium: Implications for Evaluating Risk of Chronic Beryllium Disease. *Appl. Occup. Environ. Hyg.* 16(5): 593-614. (2001).
2. **Harper, M. and M. Demange:** Concerning sampler wall deposits in the chemical analysis of airborne metals. *J. Occup. Environ. Hyg.* 4:D81-D86 (2007).
3. **Brown, C.E.:** *Filter-Paper Method for Obtaining Dust-Concentration Results Comparable to Impinger Results.* Report of Investigations, Washington, D.C.: U.S. Department of the Interior, Bureau of Mines, 1944. P. 3788.
4. **Paulus, H.J., N.A. Talvitie, D.A. Fraser, and R.G. Keenan:** Use of membrane filters in air sampling. *Am. Ind. Hyg. Assoc. Q.* 18: 267 – 273 (1957).
5. **American conference of governmental Industrial Hygienists (ACGIH):** *Air Sampling Instruments*, 1st edition, Akron, Ohio: ACGIH, 1960. PP. B-2-14, 15.
6. **Beaulieu, H.J., A.V. Fidino, L.B. Kim, M.S. Arlington, and R.M. Buchan:** A comparison of aerosol sampling techniques. “Open” versus “closed-faced” filter cassettes. *Am. Ind. Hyg. Assoc. J.* 41:758-765 (1980).
7. **Buchan, R.M. S.C. Soderholm, and M.I. Tillery:** Aerosol sampling efficiency of 37-mm filter cassettes. *Am. Ind. Hyg. Assoc. J.* 47: 825-831 (1986).
8. **International Organization for Standardization (ISO):** *Air Quality Particle Size Fraction Definitions for Health-Related Sampling* (ISO) 7708 [Standard]. Geneva: ISO, 1995.
9. **Kenny, L.C., R. Aitken, C. Chalmers, et al.:** A collaborative European study of personal inhalable aerosol sampler performance. *Am. Occup. Hyg.* 41: 135-153 (1997).
10. **Institut National de Recherche et Securite (INRS):** MetroPol. Fiche No. 003: Metauz. Metalloids, Vandoeuvre-les-Nancy, France: INRS, 2005.
11. **European Economic Community (EEC):** European Economic Community Council directive 82/605/EEC of 28 July 1982 on the protection of workers from the risks related to exposure to metallic lead and its ionic compounds at work. *Official Journal of the European Community*, 1982. P. 12.
12. **Occupational Safety and health Administration (OSHA):** Method PV2121, Gravimetric Determination. In *OSHA Sampling and Analysis Methods*. Salt Lake City, Utah: OSHA, 2003.
13. **National Institute for Occupational Safety and Health (NIOSH):** *NIOSH Manual of Analytical Methods (NMAM)*, 4th edition, Cincinnati, Ohio; NIOSH, 1994.
14. **Mark, D., and J.H. Vincent:** A new personal sampler for airborne total dust in workplaces. *Am Occup. Hyg.* 30: 89-102 (1986).
15. **Demange, M., P. Gorner, J.M. Elcabache, and R. Wrobel:** Field comparison of 37-mm closed-face filter cassettes and IOM samplers. *Appl. Occup. Environ. Hyg.* 17: 200-208 (2002).
16. **Aiken, R.J., P.E.J. Baldwin, G.C. Beaumont, L.C. Kenny, and A.D. Maynard:** Aerosol inhalability in low air movement environments. *J. Aerosol, Sci.* 30: 613-626 (1999).

- 17. Kenny, L.C., R.J. Aitken, P.E.J. Baldwin, G. Beaumont, and A.D. Maynard:** The sampling efficiency of personal inhalable aerosol samplers in low air movement environments. *J Aerosol Sci.* 30: 627-638 (1999).
- 18. Werner, M.A., T.M. Spear, and J.H. Vincent:** Investigation into the impact of introducing workplace aerosol standards based on the inhalable fraction. *Analyst* 121: 1207-1214 (1996). 0
- 19. Demange, M., J.C. Gendre, B. Hervé-Bazin, B. Carton and A. Peltier:** Aerosol evaluation difficulties due to particle deposition on filter holder inner walls. *Ann. Occup. Hyg.* 34:399-403 (1990), updated with additional data by the authors October, 2007.
- 20. Occupational Safety and Health Administration:** OSHA Sampling and Analysis Methods. Method ID215 (version 2): Hexavalent chromium. OSHA: Salt Lake City, UT; www.osha.gov/dts/sltc/methods.
- 21. Stones, F., S. Edwards, D. Crane, and G. Schultz:** The deposition of sample analyte on cassette walls. Poster presentation, American Industrial Hygiene conference & Exposition, Atlanta, Georgia, May 8-13, 2004.